

## Supporting Information

### Layered $\text{BaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}@GO$ as a High Performance Cathode for

### Calcium Ion Batteries

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## Experimental section

**Materials synthesis.** Synthesis of the  $\text{BaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$ :  $\text{BaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$  was synthesized by one-step hydrothermal method. Firstly, 0.1092 g of  $\text{V}_2\text{O}_5$  and 4.5 mL of hydrogen peroxide were dissolved in deionized water (35 mL) and stirred continuously for 30 min at room temperature. Then, 0.732 g of barium chloride was added to the above solution and continued to stir at room temperature for 2 h. Afterwards, the solution was transferred to 50 mL Teflon-lined stainless steel autoclave and reacted at  $180^\circ$  for 26 h. After cooling to room temperature, the product was washed three times with deionized water and absolute ethanol, respectively. The obtained product was dried for 12 h to obtain a red-brown  $\text{BaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$  powder, which are designated as BVO.

Synthesis of  $\text{BaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}@GO$ : Firstly, 30 mg GO was ultrasonically dispersed in deionized water (30 mL) for 3 h, 60 mg of  $\text{BaV}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$  powder was dissolved in 60 mL deionized water and continuously stirred for 20 min before being mixed with the above solution. Subsequently, the mixed solution was sonicated for another 6 h. The final

product was obtained after drying.

**Material characterization.** The crystalline structure of the obtained sample was characterized by Powder X-ray diffraction (XRD) (Rigaku D/Max X-ray diffractometer with Cu K $\alpha$  radiation) with a scan rate of 8° min<sup>-1</sup>. The surface element composition and chemical valence of BVO@GO were investigated by X-ray photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics). The TGA measurement was performed on EXSTAR TGDTA7300 under N<sub>2</sub> atmosphere at a temperature ramp of 5°C min<sup>-1</sup>. The morphologies of the final product were characterized by scanning electron microscopy (SEM, JSM-6700F, JEOL) and transmission electron microscopy (TEM, Tecnai G2 F30, FEI). The morphology and element distribution of the sample were performed on field emission scanning electron microscope (FESEM) and energy dispersive spectrometer (EDS) (Zeiss model Sigma 500).

**Electrochemical tests.** The positive electrode was composed of BVO@GO (70 wt%), Ketjen Black (20 wt%) and polyvinylidene fluoride (PVDF 10 wt%), which were mixed and dispersed in N-methyl-2-pyrrolidinone (NMP) and ground evenly. The slurry was coated on aluminum foil and dried in a vacuum drying oven at 60° for 12 h. The load of active materials on the prepared positive electrode is about 0.6~1.2 mg cm<sup>-2</sup>. We have measured the resistivity of the prepared positive electrode through the four-probe technique and its value is about 3.2  $\Omega$ ·cm. Additionally Finally, the CR2032 coin cells were assembled in an argon-filled glovebox with Whatman glass microfiber filter (GF/A) as the separator, Al foil as the collector, and ACC (1500-2500 m<sup>2</sup> g<sup>-1</sup>, GUN EI

Chemical Industry Co. Ltd) as the counter electrode. 0.8 M  $\text{Ca}(\text{TFSI})_2$  dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC), ethylmethyl carbonate (EMC) (vol/vol/vol/vol=2:3:2:3) was used as the electrolyte. Galvanostatic charge/discharge measurement was conducted with a multi-channel battery testing system (Neware CT-4008T-5V20 mA-164, Shenzhen, China). Cyclic voltammetry (CV) tests were carried out using an electrochemical workstation (CHI660E).

**Computational details:** Cambridge Serial Total Energy Package (CASTEP) was employed to finish all density functional theory (DFT) calculations in the current work. The generalized gradient approximation using Perdew–Burke–Ernzerhof functional was adopted to treat the exchange and correlation energy. The electron wave functions were expanded by a basis set of plane waves with an energy termination of 340 eV. Appropriate Monkhorst–Pack Brillouin sampling grid of spacing  $2\pi \times 0.04 \text{ \AA}^{-1}$  were used for all cases, and the convergence criterion is 0.02 meV/atom for the total energy and 0.05 eV/Å for the forces on the atoms. The diffusion barriers of  $\text{Ca}^{2+}$  in  $\text{Ba}_6\text{V}_6\text{O}_{16}$  was calculated using the periodic LST/QST method in CASTEP. The most favorable adsorption sites were chosen as the initial and final states.

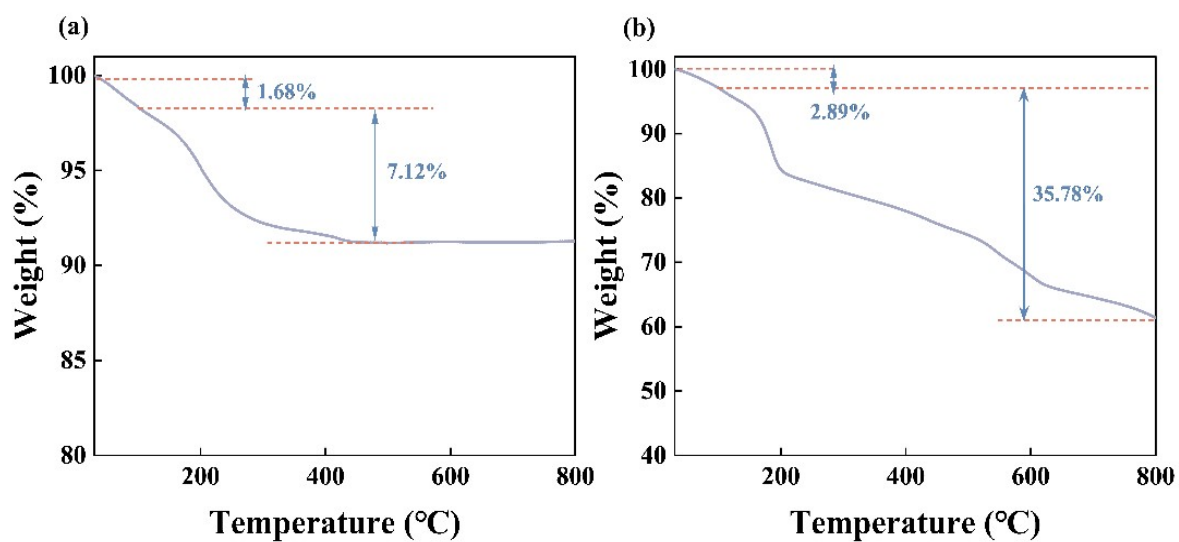


Fig. S1 TGA profiles of the as-prepared (a) BVO and (b) BVO@GO.

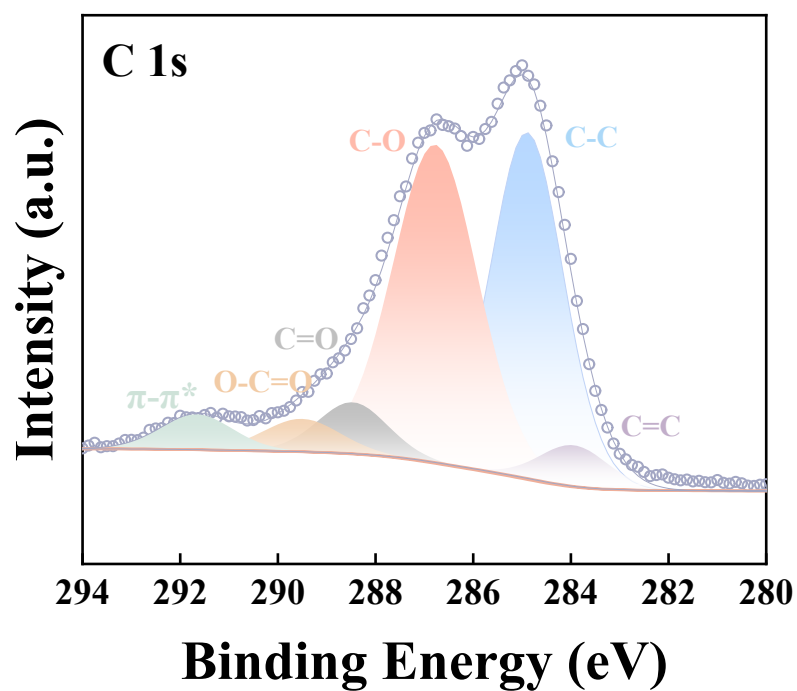


Fig. S2 XPS spectrum of C 1s for BVO@GO.

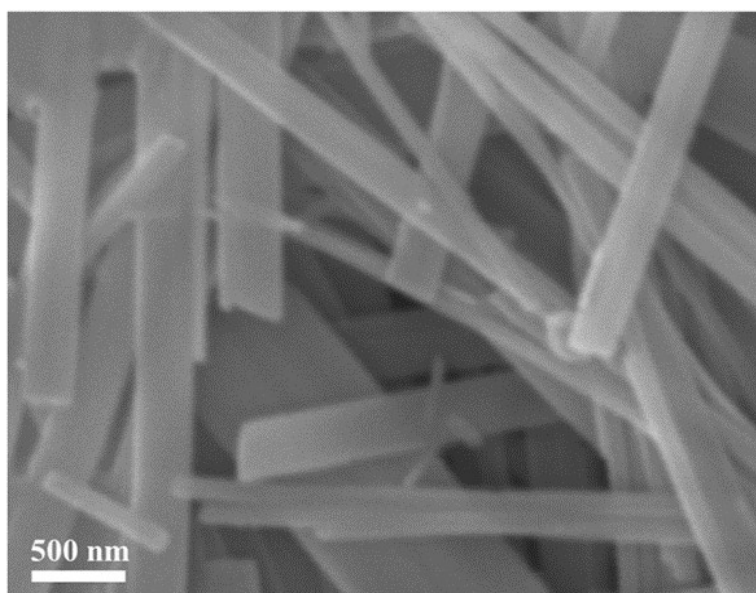


Fig. S3 SEM image of BVO.

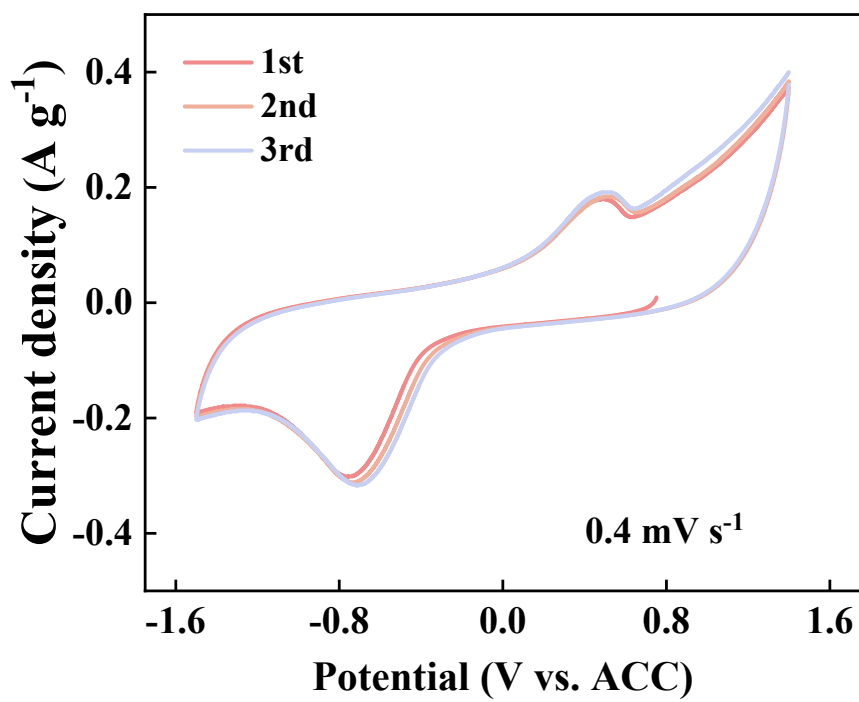
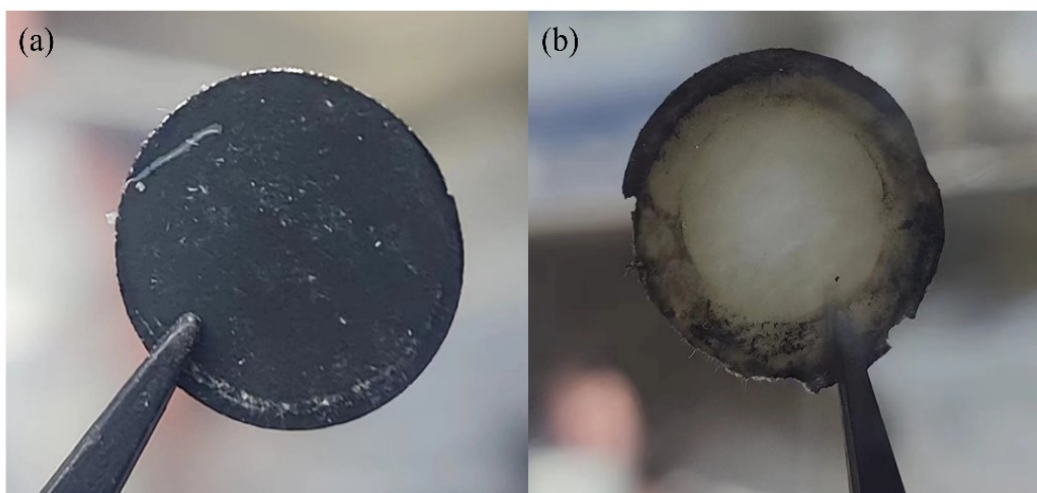


Fig. S4 CV curves at a scan rate of 0.4 mV s<sup>-1</sup>.



**Fig. S5** Digital photos of diaphragm and positive plate after 50 cycles.

**Table S1.** The Ca<sup>2+</sup> storage performance of BVO@GO and the reported inorganic cathode materials for CIBs with organic electrolyte.

Cathode	Counter	Electrolyte	Reversible (mAh g <sup>-1</sup> )	Current density (mA g <sup>-1</sup> )	Cycle number /Capacity retention	Reference
BaV <sub>6</sub> O <sub>16</sub> ·3H <sub>2</sub> O@GO	ACC	0.8 M Ca(TFSI) <sub>2</sub> in EC:DMC:PC:EMC	339.45	50	50/84%	This work
Mg <sub>0.25</sub> V <sub>2</sub> O <sub>5</sub> ·H <sub>2</sub> O	ACC	0.8 M Ca(TFSI) <sub>2</sub> in EC:DMC:PC:EMC	90	50	100/106.4%	1
K <sub>2</sub> V <sub>6</sub> O <sub>16</sub> ·2.7H <sub>2</sub> O	AC	Ca (NO <sub>3</sub> ) <sub>2</sub>	94	50	100/78.3%	2
CaV <sub>6</sub> O <sub>16</sub> ·2.8H <sub>2</sub> O	ACC	0.3 M Ca(TFSI) <sub>2</sub> in G <sub>2</sub>	131.7	50	30/94.4%	3
β-Ag <sub>0.33</sub> V <sub>2</sub> O <sub>5</sub>	AC	0.5 M Ca(BF <sub>4</sub> ) <sub>2</sub> in EC:PC	179	12.3	50/47%	4
VOPO <sub>4</sub> ·2H <sub>2</sub> O	ACC	0.8 M Ca(TFSI) <sub>2</sub> in EC:DMC:PC:EMC	100	20	35/86%	5
MnO <sub>2</sub> @PANI	AC	0.5 M Ca(TFSI) <sub>2</sub> in An	150	100	100/91.9%	6
δ-MnO <sub>2</sub>	AC	0.5 m Ca(TFSI) <sub>2</sub> electrolyte.	125	100	50/53.6%	7
CuS/C	Ca	Ca(CB <sub>11</sub> H <sub>12</sub> ) <sub>2</sub> in DME/THF	126	1000	500/92%	8
Ca <sub>0.28</sub> V <sub>2</sub> O <sub>5</sub> ·H <sub>2</sub> O:	AC	0.5 M Ca(ClO <sub>4</sub> ) <sub>2</sub>	120	30	50/74%	9
Ca <sub>x</sub> Na <sub>0.5</sub> VPO <sub>4.8</sub> F <sub>0.7</sub>	AC	0.5 M Ca(ClO <sub>4</sub> ) <sub>2</sub> in PC	65	66.6	100/92%	10
V <sub>2</sub> O <sub>5</sub>	AC	1 M Ca(ClO <sub>4</sub> ) <sub>2</sub> in ACN	150	50 (μA cm <sup>-2</sup> )	5/20%	11
Ti <sub>2</sub> O(PO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O)	AC	0.5 M Ca(BF <sub>4</sub> ) <sub>2</sub> in EC:PC	60.8	50	1500/95%	12

## Reference

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